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Supporting Information

Adhesion of Photon-driven Molecular Motors to Surfaces via 1,3-Dipolar Cycloadditions: Effect of Interfacial Interactions on Molecular Motion

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General remarks

General remarks for synthetic procedures:

Reagents were purchased from Aldrich, Acros, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. All reactions were performed in oven- or flame-dried round bottom or modified Schlenk (Kjeldahl shape) flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at 30–40 °C. Flash column chromatography was performed as described by Still et al. (Still, W. C.; Kahn, M.; Mitra, A. J. *Org. Chem.* 1978, 43, 2923-2925.) Chromatography: silica gel, Merck type 9385 230-400 mesh.

TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm).

General remarks for instrumentation:

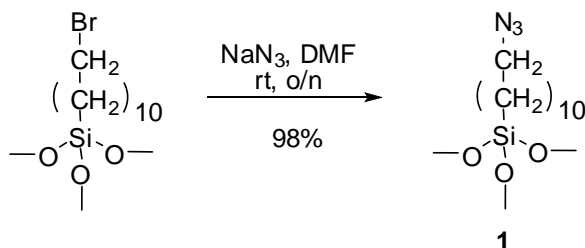
Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300, a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93, and 499.98 MHz, respectively, for the ^1H nucleus, and at 75.43, 100.57 and 124.98 MHz for the ^{13}C nucleus.

Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents CHCl_3 : δ 7.26, CDHCl_2 : δ 5.32, DMSO δ 2.5, $\text{CD}_2\text{HCO}_2\text{D}$ δ 3.31). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.0, DMSO- d_6 : δ 39.4). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet), integration, coupling constant in Hz. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at $\lambda = 365$ nm, ± 30 nm. NMR samples were placed 2-3 cm from the lamp. Solution CD spectra were recorded on a JASCO J-715 spectropolarimeter using UVASOL grade methanol in a 1.0 cm quartz cell at $T \leq -20^\circ\text{C}$ temperature. UV-vis spectra were obtained using Hewlett-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Spectroscopic ellipsometry measurements were performed on a J.A. Woollam VASE ellipsometer. Samples for analysis by XPS were prepared on silicon wafers (Wafer World Inc.) containing a thin layer of SiO_2 (approximately 2 nm, exact value measured for each sample) and measured in three different locations and the results averaged. A refractive index value of 1.5 was used for the organic layer. ATR-IR spectra of the surfaces were obtained using a Spectrum 400 FT-IR (Perkin Elmer) equipped with a Pike Veemax II attachment and a liquid nitrogen cooled MCT detector. Spectra were taken with parallel-polarized light and an incident reflection angle of 65° while samples were in intimate contact with a germanium crystal. Background spectra were taken on Si wafers containing an SiO_2 overlayer exposed to piranha solution in same manner as sample. Samples were cleaned with lens tissue immediately before measuring. Contact

angles were measured on a Data Physics contact angle goniometer. The contact angle was calculated using software provided by the company. The contact angle was measured at three different locations on each surface and the results averaged. For XPS instrumentation see below.

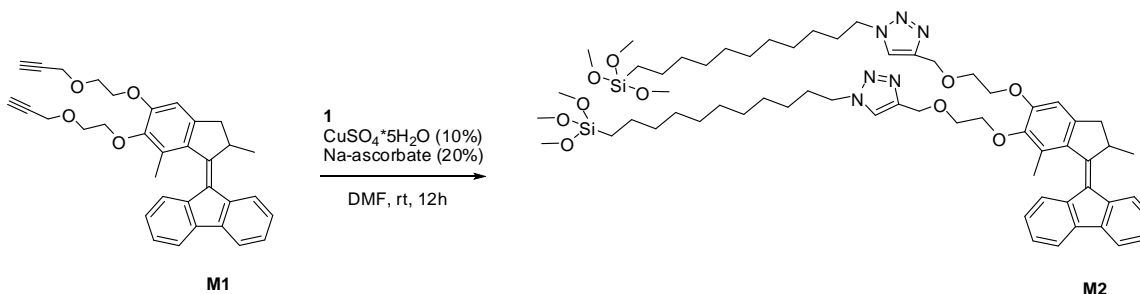
Synthesis of compounds and intermediates

1. Preparation of azidoundecyl trimethoxy silane **1**



To a solution of bromo undecyltrimethoxy silane (0.5 mL, 1.58 mmol) in DMF (3 mL) was added NaN_3 (130 mg, 2.0 mmol). After stirring overnight at rt, the reaction was quenched with water (10 mL) and the aqueous solution was extracted with Et_2O (3x10 mL). The organic phase was washed with water (2x50 mL) and brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give 490.5 mg (1.55 mmol, 98%) of a pale yellow oil. The product was used without further purification. ^1H NMR (400 MHz, CDCl_3) δ 0.62-0.66 (m, 2H), 1.26 (br s, 14H), 1.36-1.40 (m, 2H), 1.59 (quin, $J=7.2$ Hz, 2H), 3.25 (t, $J=6.8$ Hz, 2H), 3.57 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 9.0, 22.5, 26.6, 28.7, 29.0, 29.1, 29.3, 29.4, 33.0, 50.3, 50.4. (3 C could not be observed due to overlap) HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{31}\text{N}_3\text{O}_3\text{Si}$ 340.2027, found 340.2024.

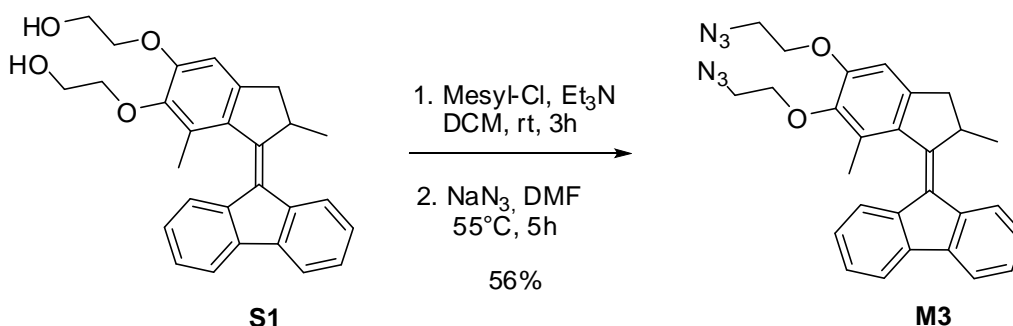
2. Preparation of triazolsilane-motor **M2**



To a solution of dialkyne motor **M1**¹ (50 mg, 0.1 mmol) in DMF (5 mL) were added **1** (92 mg, 0.3 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.5 mg, 0.01 mmol) and Na-ascorbate (4 mg, 0.02 mmol) each predissolved in DMF (0.5 mL). After stirring the mixture overnight at rt water (25

mL) was added. The aqueous solution was extracted with EtOAc (3x20 mL). The combined organic phase was washed with water (2x50 mL) and brine (30 mL) and dried (Na₂SO₄). The crude mixture was purified by flash chromatography (SiO₂, EtOAc) to give 21 mg of a semi-solid (0.018 mmol, 18%) which was used immediately for surface modifications. ¹H NMR (400 MHz, CDCl₃) δ 0.61-0.65 (m, 4H), 1.21-1.43 (m, 35H), 1.80-1.89 (m, 4H), 2.18 (s, 3H), 2.52 (d, *J* = 14.4 Hz, 1H), 3.28 (dd, *J* = 4.4, 14.8 Hz, 1H) 3.56 (s, 18H), 3.87-3.90 (m, 2H), 3.97 (t, *J* = 4.4 Hz, 2H), 4.20-4.35 (m, 9H), 4.76 (d, *J* = 6 Hz, 4H), 6.83 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.32-7.35 (m, 4H) 7.51 (s, 1H, *triazole-H*), 7.60 (s, 1H, *triazole-H*), 7.74 (d, *J* = 7.6 Hz, 1H), 7.79-7.81 (m, 1H), 7.84-7.86 (m, 1H). HRMS (TOF) calcd for C₆₂H₉₄N₆O₁₀Si₂ 1139.6642, found 1139.6657.

3. Preparation of diazide-motor M3

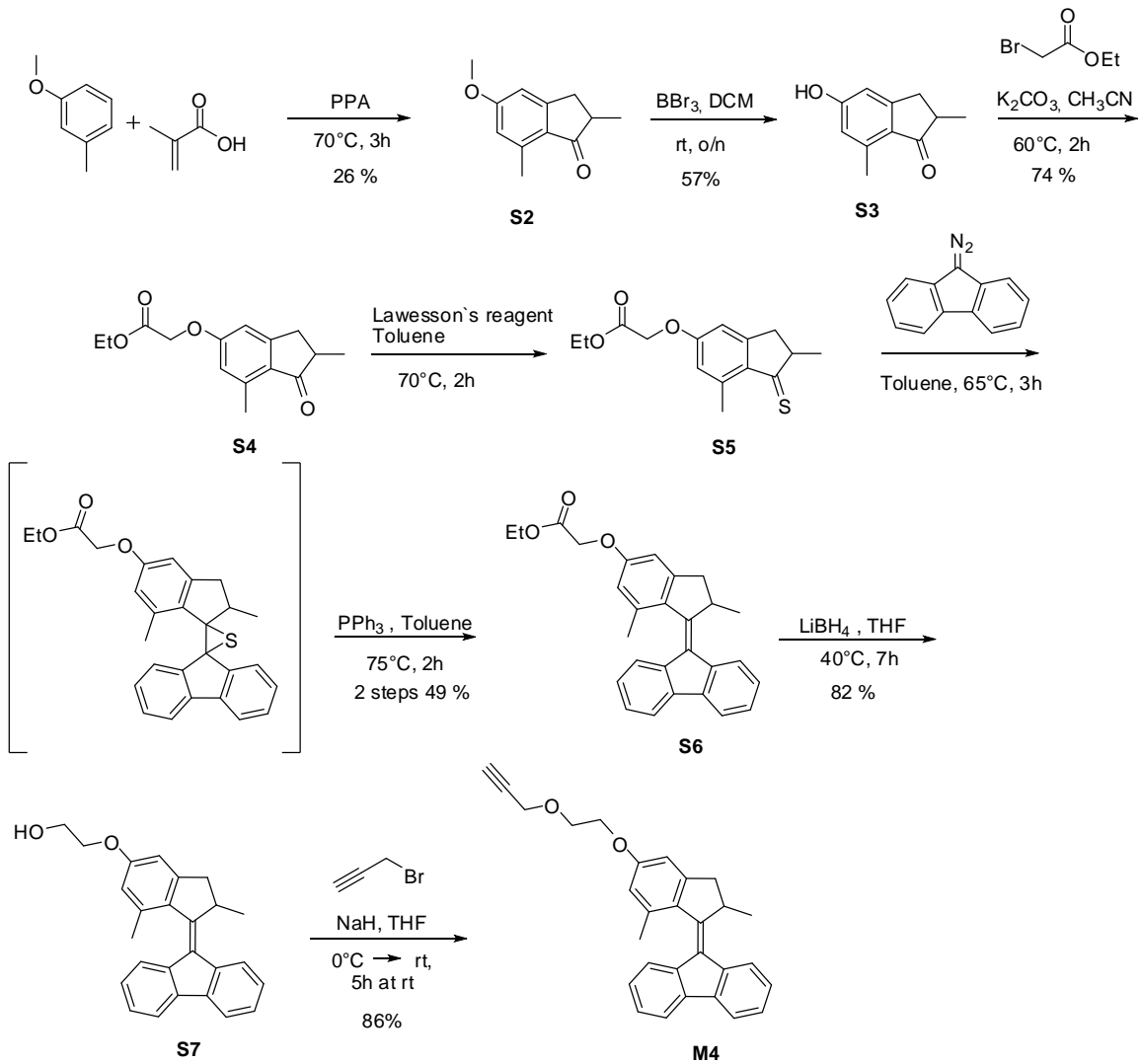


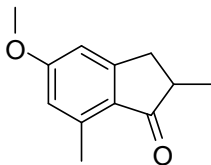
To a mixture of diol motor **S7**² (50 mg, 0.117 mmol) and triethylamine (100 μL) in dichloromethane (5 mL) cooled to 0°C, were added methanesulfonyl chloride (28 μL, 0.350 mmol) and the solution was allowed to warm to rt. After 3h at rt the mixture was poured on ice-cold 1 M aq. HCl-solution (20 mL). The mixture was extracted with dichloromethane (3x20 mL), washed with saturated aq. NaHCO₃-solution (2x30 mL) and dried (Na₂SO₄). After evaporation of the solvent at reduced pressure the residue was dissolved in DMF (5 mL), NaN₃ was added (46 mg, 0.7 mmol) and the mixture was stirred at 55°C for 5h. The reaction was quenched with water (10 mL) and the mixture was extracted with ethyl acetate (3x10 mL). The organic phase was washed with water (20 mL) and brine (20 mL) and dried (Na₂SO₄). The solvent was evaporated at reduced pressure and the crude product was purified by flash chromatography (SiO₂, *n*-heptane : ethyl acetate 3 : 1) to give a yellow solid (31 mg, 0.065 mmol, 56%).

¹H NMR (400 MHz, CD₂Cl₂) δ 1.32 (d, *J* = 6.8 Hz, 3H), 2.20 (s, 3H), 2.57 (d, *J* = 14.4 Hz, 1H), 3.31 (dd, *J* = 5.6, 14.4 Hz, 1H), 3.62 (br, t, 2H), 3.73 (br, t, 2H), 4.10-4.17 (m, 2H), 4.19-4.30 (m, 3H), 6.90 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.33-7.37 (m, 3H), 7.77 (d, *J* = 8 Hz, 1H), 7.80-7.83 (m, 1H), 7.87-7.89 (m, 1H);

¹³C NMR (APT, 100 MHz, CDCl₃) δ 15.9, 18.9, 41.5, 44.8, 50.5, 51.3, 67.4, 71.1, 108.2, 119.2, 119.6, 123.3, 123.7, 126.5, 126.7, 126.8, 127.0, 129.3, 132.1, 134.3, 137.8, 139.3, 139.6, 139.7, 143.6, 145.1, 151.4, 152.2. HRMS (EI) calcd for C₂₈H₂₆N₆O₂ 478.2117, found 478.2125.

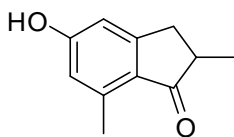
4. Preparation of molecular motor M4





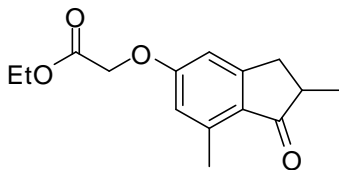
5-methoxy-2,7-dimethyl-2,3-dihydro-1H-indene-1-one S2

To polyphosphoric acid (30 mL) stirred and heated at 70°C, were added methacrylic acid (5.2 mL, 60.5 mmol) and 3-methylanisole (5.2 mL, 40.9 mmol). After stirring at 70°C for 3 h, the mixture was poured onto ice and stirred overnight. The water layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with aqueous NaHCO₃ (30 mL), water (30 mL) and brine (30 mL) and dried (Na₂SO₄). After evaporation of the solvent the crude product was purified by flash chromatography (SiO₂, *n*-heptane : EtOAc = 3 : 1) to give 2.0 g (10.5 mmol, 26 %) of a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.27 (d, *J* = 7.2 Hz, 3H), 2.60 (s, 3H), 2.60-2.71 (m, 2H), 3.28 (q_{apparent}, *J* = 8.4 Hz, 1H), 3.84 (s, 3H) 6.63 (s, 1H), 6.70 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 16.5, 18.2, 34.7, 42.3, 55.3, 107.3, 116.3, 127.3, 140.8, 156.9, 164.5, 208.1. HRMS (EI) calcd for C₁₂H₁₄O₂ 190.0994, found 190.0989.



5-hydroxy-2,7-dimethyl-2,3-dihydro-1H-indene-1-one S3

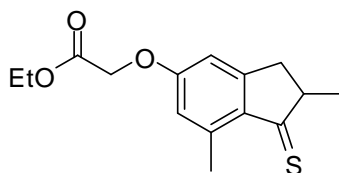
BBr₃ (0.2 mL, 2.1 mmol) was added slowly to a stirred solution of **S2** (200 mg, 1.0 mmol) in CH₂Cl₂ (3 mL) at 0°C under inert atmosphere (N₂). The mixture was allowed to warm up to rt and stirred overnight at rt. The reaction was quenched by adding water (3 mL) slowly. The water layer was extracted with ethyl acetate until the water phase became colorless. The organic layer was washed with water (10 mL) and brine (10 mL), and dried (Na₂SO₄). The solvent was evaporated under reduced pressure to give the crude product as a brown solid. The solid was suspended in diethyl ether (2 x 10 mL) followed by filtration to give 105.0 mg (0.6 mmol, 57 %) of pale brown solid. ¹H NMR (400 MHz, Methanol-*d*₄) δ 1.22 (d, *J* = 7.6 Hz, 3H), 2.50 (s, 3H), 2.53-2.65 (m, 2H), 3.26 (q_{apparent}, *J* = 8.4 Hz, 1H), 6.55 (s, 1H), 6.63 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 16.3, 17.8, 33.8, 41.6, 109.6, 116.8, 125.2, 139.8, 157.1, 162.9, 206.9. HRMS (EI) calcd for C₁₁H₁₂O₂ 176.0837, found 176.0823.



Ethyl 2-(2,7-dimethyl-1-oxo-2,3-dihydro-1H-indene-5-yloxy)acetate **S4**

To a solution of **S3** (100.0 mg, 0.57 mmol) in acetonitrile (5 mL) were added K_2CO_3 (150.0 mg, 1.1 mmol) and ethyl bromoacetate (95 μ L, 0.86 mmol) and the mixture was heated at 60°C for 2h. The reaction was quenched by the addition of water (10 mL). The mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), and dried (Na_2SO_4). After the evaporation of the solvent the crude product was purified by flash chromatography (SiO_2 , *n*-heptane : EtOAc = 3 : 1) to afford 110.0 mg (0.42 mmol, 74 %) of white crystals.

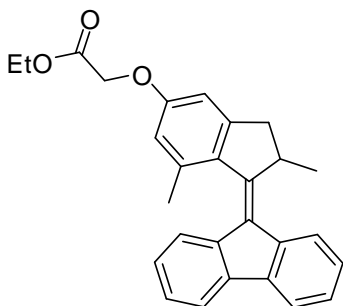
Mp 78.5-79.0 °C; 1H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 2.59 (s, 3H), 2.62-2.68 (m, 2H), 3.27 (q_{apparent}, J = 8.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.66 (s, 2H), 6.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 16.4, 18.3, 34.5, 42.3, 61.4, 65.0, 107.9, 116.6, 128.0, 141.0, 156.9, 162.3, 168.1, 208.2. HRMS (EI) calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1200.



Ethyl 2-(2,7-dimethyl-1-thioxo-2,3-dihydro-1H-indene-5-yloxy)acetate **S5**

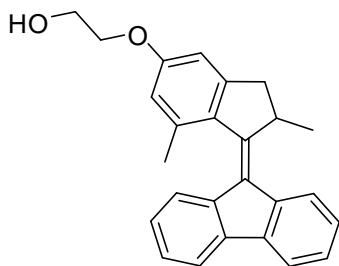
Lawesson's reagent (465.4 mg, 1.15 mmol) was added to a solution of **S4** (200 mg, 0.76 mmol) in toluene (10 mL). The mixture was heated at 70°C for 3 h and filtered through a plug of celite. The solid residue was washed with toluene. The filtrate was concentrated *in vacuo* and purified by flash chromatography (SiO_2 , *n*-pentane : diethyl ether = 1 : 1) to give a purple oil which was used immediately in the next step. (*Note*: this compound is not stable towards air or moisture and slowly decomposes to ketone **S4**.)

1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 6.8 Hz, 3H), 1.41 (d, J = 7.2 Hz, 3H), 2.75 (s, 3H), 2.79 (d, J = 2.8 Hz, 1H), 3.02 (dq_{in}, J = 3.2, 7.2 Hz, 1H), 3.37 (dd, J = 17.4, 7.2 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.69 (s, 2H), 6.69 (s, 1H), 6.74 (s, 1H).



Ester-motor **S6**

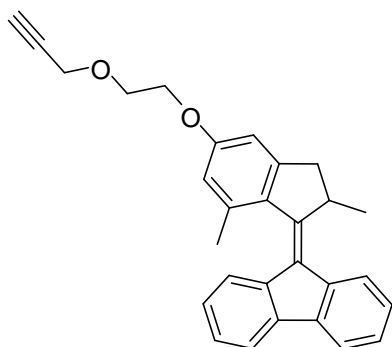
Diazofluorenone² (300 mg, 1.56 mmol) was added to a solution of **S5** in toluene (10 ml). The mixture was heated up to 65°C for 3 h. The formation of the episulfide was monitored by ¹H NMR spectroscopy by following the appearance of the upper-half aromatic protons of the episulfide at 6.42 ppm and 6.55 ppm. To the episulfide solution PPh₃ (350 mg, 1.35 mmol) was added and the mixture was heated for an additional 2 h at 75°C. The reaction mixture was concentrated *in vacuo*. Et₂O (20 ml) was added to the mixture to precipitate PPh₃S as yellow crystals. The precipitate was filtered and the procedure was repeated once more. The resulting Et₂O solution was concentrated to ~20 mL and CH₃I (0.5 ml, 8.0 mmol) was added. The mixture was stirred for 2 h at rt to precipitate the residual PPh₃ which was removed by filtration. After evaporation of the solvent the crude product was purified by flash chromatography (SiO₂, *n*-heptane : ethyl acetate = 5 : 1) to give alkene **5** as a yellow solid (150 mg, 0.37 mmol, 49% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 1.32-1.36 (m, 6H), 2.26 (s, 3H), 2.57 (d, *J* = 14.8 Hz, 1H), 3.33 (dd, *J* = 6.4, 14.8 Hz, 1H), 4.14 (quin, *J* = 5.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.69 (s, 2H), 6.71 (s, 1H), 6.81 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.34-7.39 (m, 3H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.80-7.82 (m, 1H), 7.86-7.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 18.8, 21.6, 41.5, 44.7, 61.3, 65.4, 109.2, 114.8, 119.1, 119.6, 123.3, 123.6, 126.4, 126.5, 126.7, 126.8, 129.0, 134.0, 137.8, 138.8, 139.2, 139.5, 139.6, 149.4, 151.3, 158.9, 168.8 HRMS (EI) calcd for C₂₈H₂₆O₃ 410.1882, found 410.1877.



Alcohol-motor **S7**

A solution of **S6** (115 mg, 0.28 mmol) in THF (5 mL) was added to a suspension of LiBH₄ (20 mg, 0.52 mmol) in THF (5 mL) and the mixture was stirred at 40°C for 7 h. The reaction was quenched with aqueous HCl solution (5 mL, 0.1 M) and the mixture

was extracted with EtOAc until the aqueous phase was colorless. The combined organic layers were washed with water (10 mL) and brine (10 mL) and dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (SiO₂, *n*-heptane : ethyl acetate = 1 : 1) to give 85 mg (0.23 mmol, 82 %) yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 1.32 (d, *J* = 6.8 Hz, 3H), 2.04 (t, *J* = 6 Hz, 1H OH), 2.25 (s, 3H), 2.58 (d, *J* = 14.4 Hz, 1H), 3.32 (dd, *J* = 6.0, 13.2 Hz, 1H), 4.01 (q, *J* = 5.2 Hz, 2H), 4.13 (quin., *J* = 6.8 Hz, 1H), 4.18 (q, *J* = 4.8 Hz, 2H), 6.72 (s, 1H), 6.83 (s, 1H), 7.15 (t, *J* = 6.4 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.34-7.39 (m, 3H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.80-7.84 (m, 1H), 7.85-7.90 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.9, 21.6, 41.5, 44.6, 61.4, 69.2, 109.1, 114.6, 119.1, 119.6, 123.3, 123.6, 126.4, 126.5, 126.7, 128.8, 133.4, 137.9, 138.8, 139.2, 139.6, 149.4, 151.6, 159.8. (2 C not observed due to overlap) HRMS (EI) calcd for C₂₆H₂₄O₂ 368.1776, found 368.1751.



Alkyne-motor **M4**

A suspension of NaH (70 mg, 1.5 mmol, 50% in oil) in THF (3 mL) was cooled to 0°C and a solution of **S7** (85 mg, 0.23 mmol) in THF (7 mL) was added dropwise (under N₂ atmosphere). To this mixture propargyl bromide (0.1 mL, 0.90 mmol, 80 % in toluene) was added. The solution was stirred at room temperature for 5 h. The reaction was quenched with water (10 mL) and the mixture was extracted with EtOAc until the yellow color of the aqueous phase had disappeared. The organic phase was washed with water (10 mL) and brine (10 mL) and dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (SiO₂, *n*-heptane : ethyl acetate = 7 : 1) to give yellow crystals (80 mg, 0.20 mmol, 86 %). ¹H NMR (400 MHz, CDCl₃) δ 1.32 (d, *J* = 6.4 Hz, 3H), 2.24 (s, 3H), 2.49 (t, *J* = 2.4 Hz, 1H), 2.57 (d, *J* = 14.8 Hz, 1H), 3.32 (dd, *J* = 6.0, 14.6 Hz, 1H), 3.96 (t, *J* = 5.2 Hz, 2H), 4.13 (quin., *J* = 6.4 Hz, 1H), 4.20-4.28 (m, 2H), 4.32 (dd, *J* = 1.2, 2.4 Hz, 2H), 6.72 (s, 1H), 6.83 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.33-7.39 (m, 3H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.80-7.84 (m, 1H), 7.85-7.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 21.6, 41.5, 44.6, 58.5, 67.2, 68.1, 74.8, 109.1, 114.7, 119.1, 119.6, 123.3, 123.6, 126.4, 126.5, 126.70, 126.73, 128.7, 133.3, 137.9, 138.8, 139.1, 139.5, 149.3, 151.8, 159.9. (2 C not observed due to overlap) HRMS (EI) calcd for C₂₉H₂₆O₂ 406.1933, found 406.1925.

Irradiation experiments to generate unstable isomers of motors **M3** and **M4**

Molecular motors **M3** (diazide) and **M4** (monoacetylene) (2 mg) were dissolved in CD₂Cl₂ (~1 ml). These samples were placed in an NMR tube and irradiated with 365 nm light at -60° C at a distance of 2-3 cm from the centre of the lamp. ¹H-NMR spectra of the samples were taken before, during and after irradiation at -50° C. No further changes were observed after 6 h of irradiation. After warming the samples to room temperature, only the stable form was observed by ¹H-NMR.

Stable-M3: ¹H NMR (500 MHz, -50°C, CD₂Cl₂) δ 1.26 (d, 3H, *J*= 5.5 Hz), 2.15 (s, 3H), 2.54 (d, *J*=14.5 Hz, 1H), 3.25 (dd, *J*= 4, 13.8 Hz, 1H), 3.50-3.61 (br, m, 2H), 3.63-3.70 (br, m, 1H), 3.70- 3.78 (br, m, 1H), 4.01-4.12 (br, m, 2H), 4.12-4.19 (br, m, 1H), 4.19-4.28 (br, m, 2H), 6.87 (s, 1H), 7.12 (t, *J*= 7.0 Hz, 1H), 7.27 (d, *J*= 7.5Hz, 2H), 7.31-7.38 (m, 2H), 7.76 (d, *J*= 7.0 Hz, 1H), 7.78-7.83 (m, 1H), 7.83-7.88 (m, 1H)

Unstable-M3: ¹H NMR (500 MHz, -50°C, CD₂Cl₂) δ 1.46 (d, *J*= 5.5 Hz, 3H), 2.00 (s, 3H), 2.90 (dd, *J*= 5.5, 15.5 Hz, 1H), 3.36-3.41 (m, 1H), 3.53-4.22 (peaks in this region could not be resolved due to overlap with remaining stable-**5**), 6.81 (s, 1H), 7.15 (t, *J*= 7 Hz, 1H), 7.23-7.35 (peaks in this region could not be resolved due to overlap with remaining stable-**5**), 7.65-7.71 (m, 1H), 7.75-7.87 (peaks in this region could not be resolved due to overlap with remaining stable-**5**)

Stable-M4: ¹H NMR (500 MHz, -50°C, CD₂Cl₂) δ 1.29 (d, *J*= 6.5 Hz, 3H), 2.20 (s, 3H), 2.61 (d, *J*= 15 Hz, 1H), 2.64 (t, *J*= 2.0 Hz, 1H), 3.30 (dd, *J*= 5.5, 14.8 Hz, 1H), 3.92 (br, t, 2H), 4.12 (quin, *J*= 6.0 Hz, 1H), 4.18-4.21 (m, 2H), 4.31 (br, d, 2H, *J*= 1.6 Hz), 6.72 (s, 1H), 6.84 (s, 1H) 7.18 (t, *J*= 7.5 Hz, 1H), 7.31-7.36 (m, 2H), 7.37-7.41 (m, 2H), 7.81 (d, *J*= 7.5Hz, 1H), 7.84-7.86 (m, 1H), 7.89-7.90 (m, 1H)

Unstable-M4: ¹H NMR (500 MHz, -50°C, CD₂Cl₂) δ 1.50 (d, , *J*= 6.0 Hz, 3H), 2.04 (s, 3H), 3.00 (dd, *J*= 6, 16.3 Hz, 1H), 3.40-3.45 (m, 1H) 3.92-4.31 (peaks in this region could not be resolved due to overlap with remaining stable-**4**), 6.67 (s, 1H), 6.79 (s, 1H) 7.18-7.90 (peaks in this region could not be resolved due to overlap with remaining stable-**4**).

Materials and methods (surfaces)

Quartz microscope slides were obtained from UQG Optics. Toluene and THF were reagent grade and were dried and distilled before use according to standard procedures. Other solvents used were reagent grade chemicals (LAB-SCAN analytical sciences, Poland), and were used as received. All water and aqueous solutions used with surfaces were doubly distilled.

Silicon wafers: XPS analysis on insulating surfaces (like quartz) generates surface charging. Since compensation with a flood gun rapidly destroys organic molecules, the charging effect was minimized by employing a very thin SiO_x layer on a conducting silicon substrate which mimics the quartz surface.³

Experimental procedures for surface modification

11-azidoundecyltrimethoxysilane monolayer on quartz

Quartz microscope slides were cut into pieces so as to fit into the measurement cell of the UV/Vis spectrometer. They were cleaned using a 3/7 ratio of 30% H₂O₂ in H₂SO₄ (*Caution! This mixture is extremely corrosive and reactive toward organics*) at 80 °C. These samples were then rinsed with water (3 times) and with MeOH and dried under a stream of N₂.

Azide-terminated monolayer was prepared according to two different methods:

Method A (Assembly in toluene without pre-hydrolysis)

Piranha-cleaned quartz slides were immersed in a 1 mM solution of the silane in distilled toluene for 1 d at rt. After the assembly the slides were sonicated twice in fresh toluene and once in MeOH, 2 min each, and dried under a stream of N₂.

Method B (Assembly in cyclohexane after exposure to hydrolysis environment)

1.25 mL of a hydrolysis solution containing 0.04 g 11-azidoundecyltrimethoxy silane, 6 ml distilled THF, 31 µl double-distilled H₂O and 4 µl 37% aq. HCl was added to 25 mL cyclohexane to give a slightly hazy solution. The piranha-cleaned quartz slides were immersed into this solution. In general slides were left immersed overnight, however, the surface modification was found to be complete within approximately 4 h. After the assembly the slides were sonicated in DMF, toluene and MeOH for 2 min each and dried under a stream of N₂.

Attaching M1 to azide-functionalized surfaces:

Compound **M1** was grafted to the azide monolayer in DMF at room temperature by immersing the slide into a 2 mM solution of **1** containing 1 mol% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 5 mol% Na-ascorbate relative to the alkyne moieties. Although the reaction time depended on the method of preparing the azide surface slides were typically immersed for 12 h. The modified quartz substrate or silicon wafer was sonicated in DMF, water and MeOH for 2 min each, and then dried under a stream of N_2 .

Higher coverages were obtained when the motor was reacted with azide surfaces prepared by *Method B*.

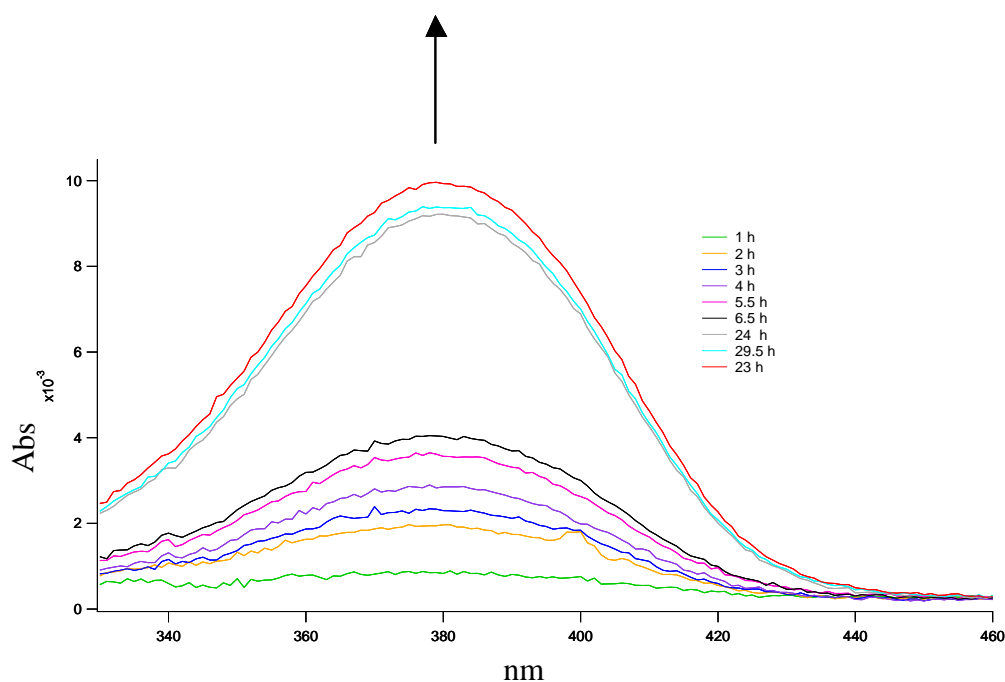


Figure S1: UV-Vis absorption spectra of **MS1** after reaction with SAM 1 for various amounts of time. The signal increases with reaction time.

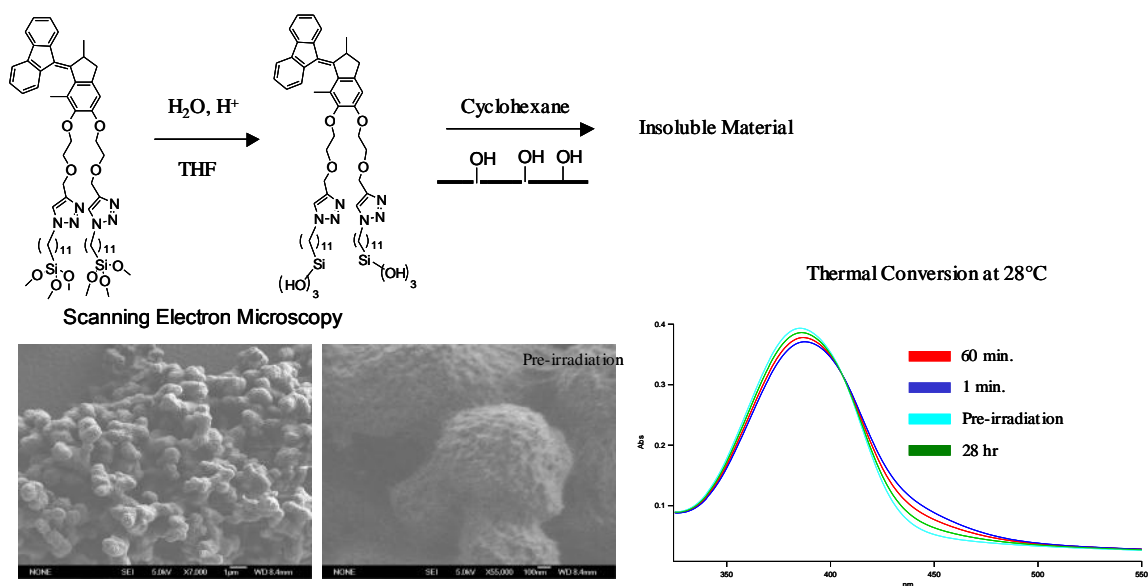


Figure S2: Addition of a solution of **M2** in THF to cyclohexane results in the evolution of an insoluble precipitate. A multilayer film binds tenaciously to quartz. SEM images of the film are shown. The film shows a UV-Vis absorption signal comparable to the spectrum of the **M1** in solution. Irradiation of the film results in a red-shift of the UV-Vis signal as found for the motor in solution and when attached to a surface as a monolayer.

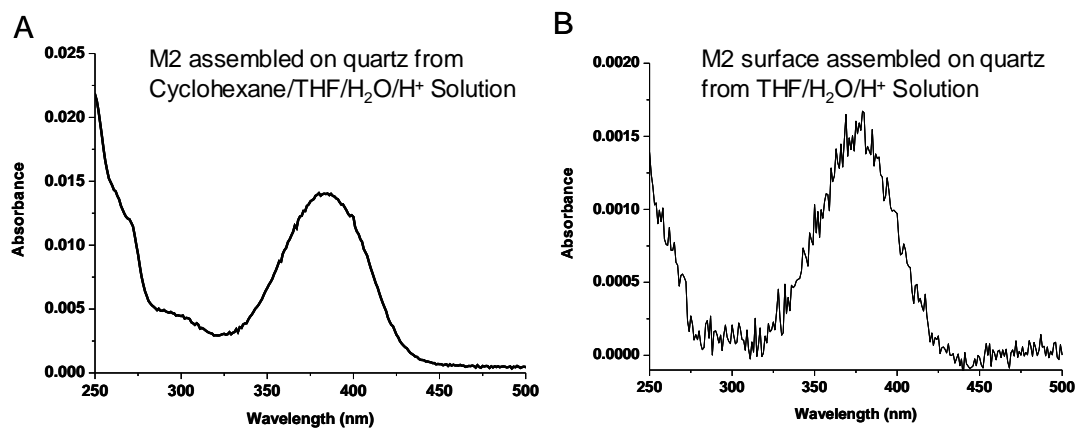


Figure S3: Mono- to submonolayer films of **M2** assembled on quartz. A) **M2** self-assembled from a 0.01 mM solution of **M2** in cyclohexane/THF/H₂O/H⁺ solution. B) **M2** self-assembled from a 0.01 mM solution of **M2** in THF/H₂O/H⁺.

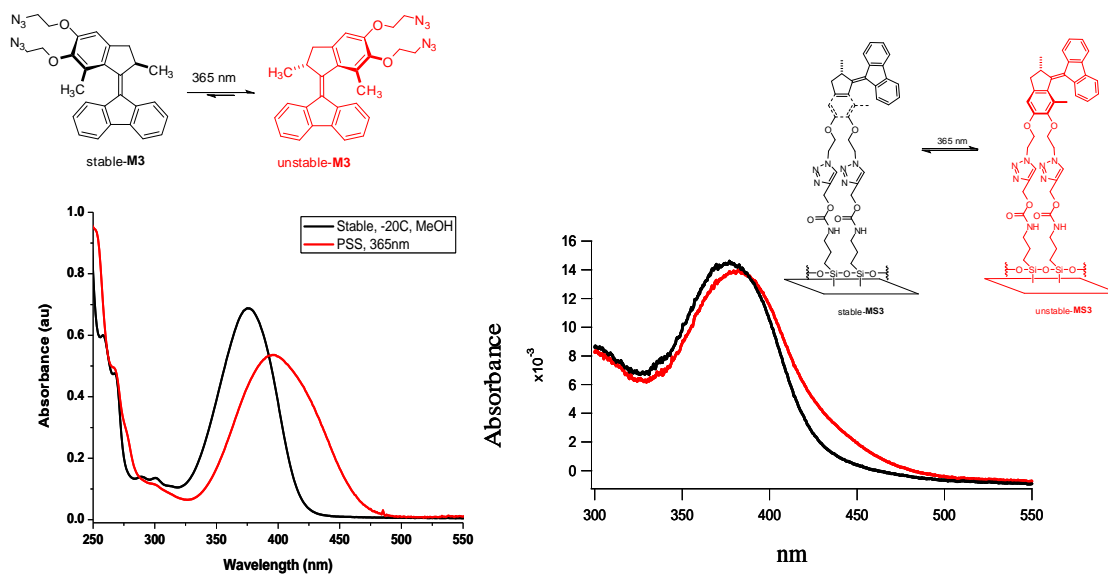


Figure S4: UV-Vis spectra of **M3** in MeOH (irradiation at -20°C) (left) and **MS3** on quartz (irradiation at rt). The black spectra correspond to the stable form of the motor. The red spectra correspond to the unstable form.

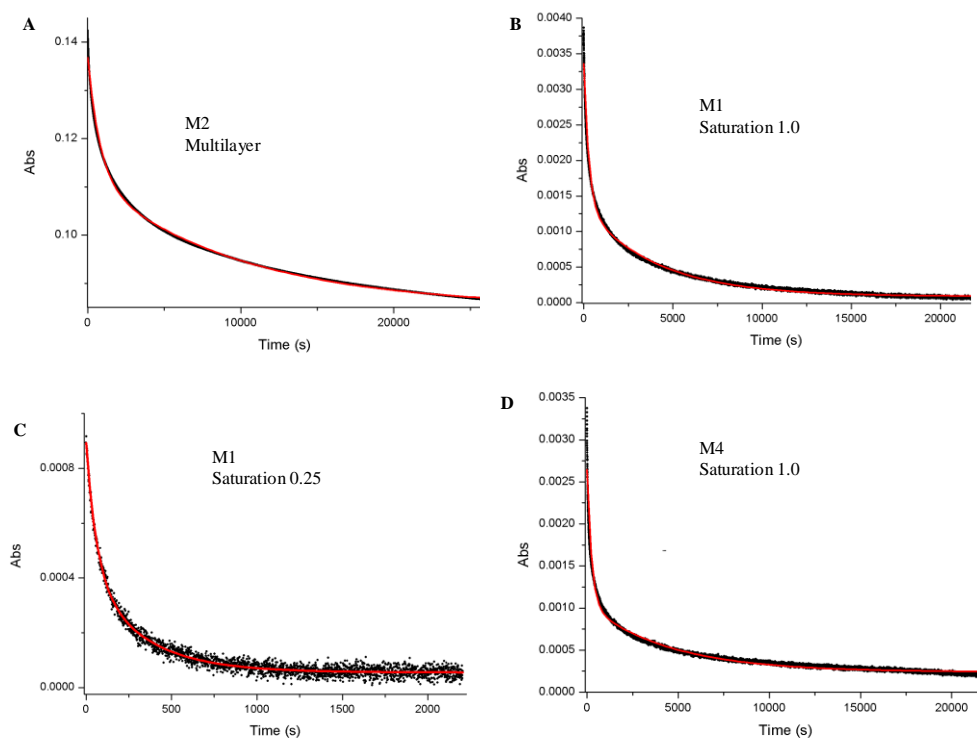


Figure S5: Thermal decay at 25° C of UV-Vis signal at 439 nm during thermal isomerization of the motors. Each curve was fit with a biexponential decay. (A) **M2** multilayer; (B) **M1**, saturation coverage 1.0; (C) **M1**, saturation coverage 0.25; (D) **M4**, saturation coverage 1.0

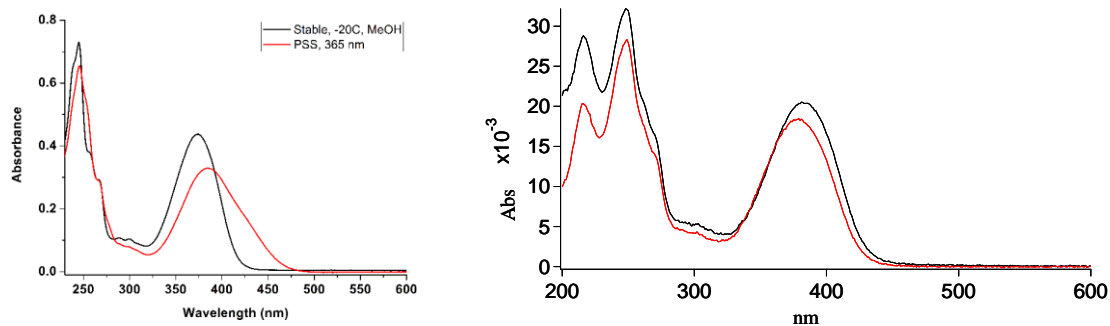


Figure S6: UV-Vis spectra. Left: Stable and unstable form of **M4** in methanol. Right: **MS1** (black) and **MS4** (red)

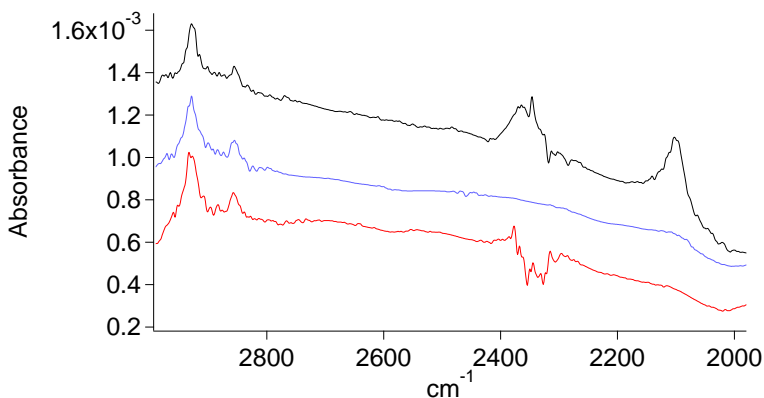


Figure S7: IR spectra of **SAM 1** (black), **MS1** (red) and **MS4** (blue)

XPS measurements

For the X-ray photoelectron spectroscopy (XPS) measurements, the samples were introduced through a load lock system into an SSX-100 (Surface Science Instruments) photoemission spectrometer with a monochromatic Al K α X-ray source ($h\nu=1486.6$ eV). The base pressure in the spectrometer during the measurements was 10^{-10} mbar. The photoelectron takeoff angle was 37° . The energy resolution was set to 1.3 eV to minimize measuring time. XPS binding energies were referenced to the Si 2p core level set to the SiO₂ reference value of 103.0 eV.⁴ Spectral analysis included a linear background subtraction and a peak deconvolution that employed mixed Gaussian-Lorentzian functions in a least-square curve-fitting program (WinSpec) developed at the LISE, University of Namur, Belgium. For each sample, a survey scan and the C 1s, O 1s, N 1s and Si 2p narrow scan spectra were collected. The photoemission peak areas of each element, used to estimate the amount of each species on the surface, were normalized by the sensitivity factors of each element tabulated for the spectrometer used. Four different points on each sample were analyzed to check for homogeneity of the monolayer. The same elemental composition for all points of the same sample was obtained, suggesting that all samples were homogeneous.

XPS of 11-azidoundecyltrimethoxysilane monolayer on silicon wafers

The survey scan of the azide (**1**) self-assembled monolayer (**SAM 1**) (**Figure S8**) shows the core levels of silicon, carbon, nitrogen and oxygen. The presence of the carbon and the nitrogen peaks is clear evidence of the modification of the surface with the azide. The

ratio of the peak areas of carbon 1s and nitrogen 1s matches the stoichiometry of the 11-azidoundecyltrimethoxysilane, namely 11 to 3.

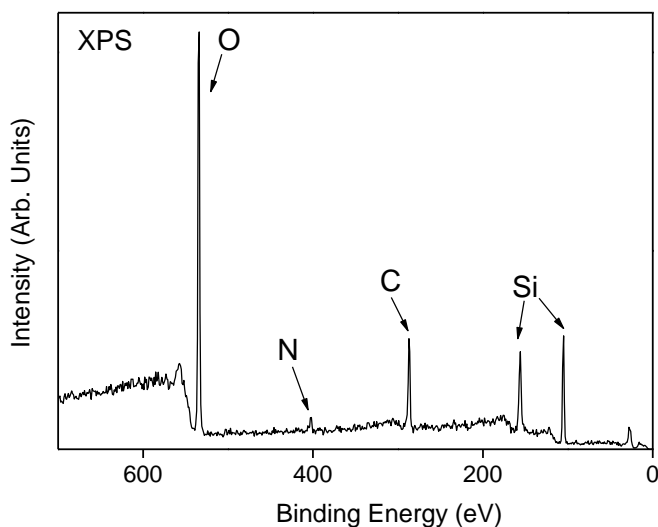


Figure S8: X-ray photoelectron survey spectrum of the azide **SAM 1** on silicon oxide.

XPS of M4 after 1,3-dipolar cycloaddition on azide-modified silicon wafers

Figure S9 represents the XPS survey spectrum of 1-legged molecular motor **M4** after 1,3-dipolar cycloaddition on an azide-modified silicon wafer. The absence of a copper peak at 933 eV, sulphur peak at 164 eV and sodium peak at 1072 eV indicates the elimination of the catalyst and the ascorbate after the formation of the dialkyne-motor monolayer.

Comparing the survey spectrum before (Fig. S8) and after (Fig. S9) the alkyne-motor attachment, we can see an increase in the intensity of the carbon peak, which corresponds with the motor monolayer on the surface.

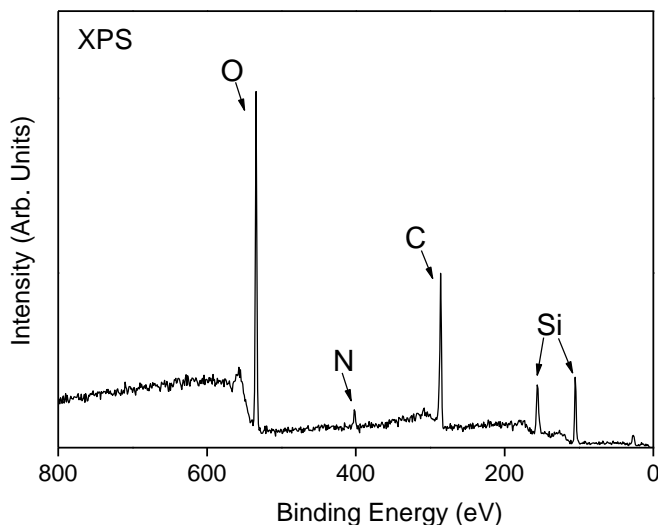


Figure S9: X-ray photoelectron survey spectrum of **M4** after 1,3-cycloaddition on azide-modified silicon wafers.

Figure S10 (upper panel) presents the N1s core level spectrum of the azide-modified silicon wafer with three distinct components: the peak at 405 eV binding energy corresponds to the electron deficient nitrogen atom in the middle of the azide group. The peaks at 402 and 401.2 eV are attributed to neutral and electron rich nitrogen atoms, respectively.⁵⁻⁷ **Figure S10** (lower panel) shows the nitrogen spectrum after the reaction of the azide monolayer with the 1-legged alkyne motor **M4** via the 1,3-dipolar cycloaddition, and has four components: the first three peaks at 400.4, 401.4 and 402.5 eV binding energy correspond to the new triazole-compound created through the 1,3-dipolar cycloaddition. The peak at 405 eV (6%) is attributed to the presence of azide groups that did not react.

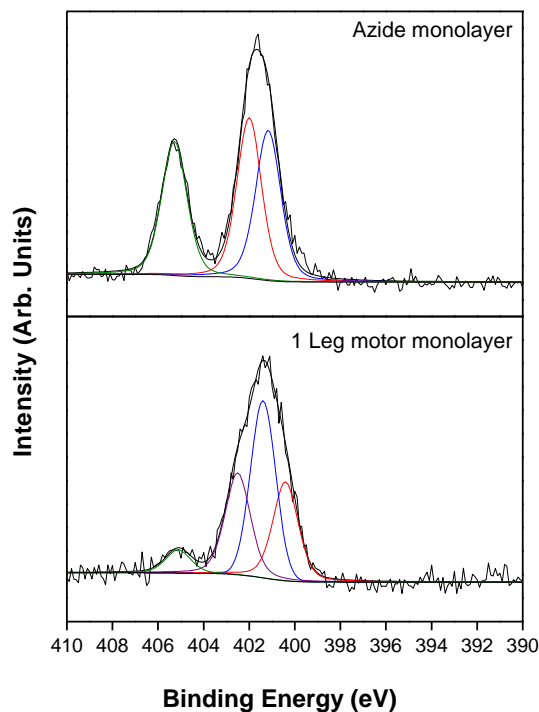
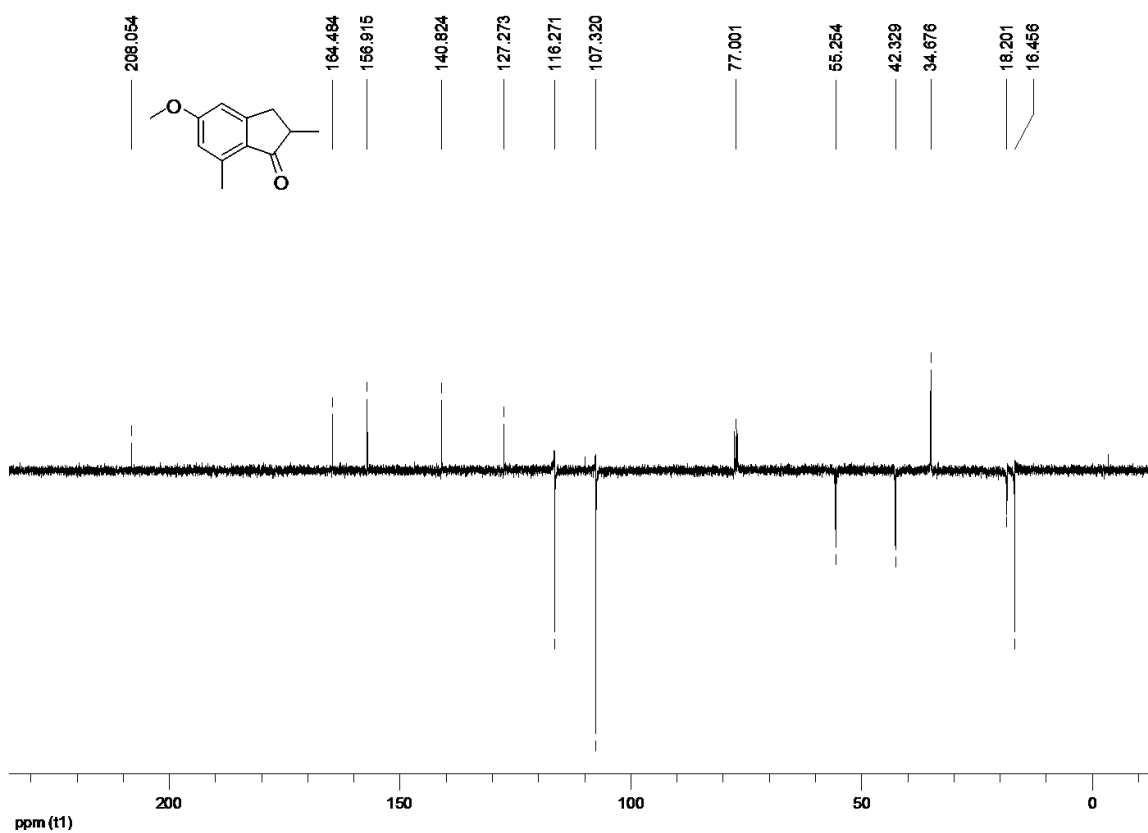
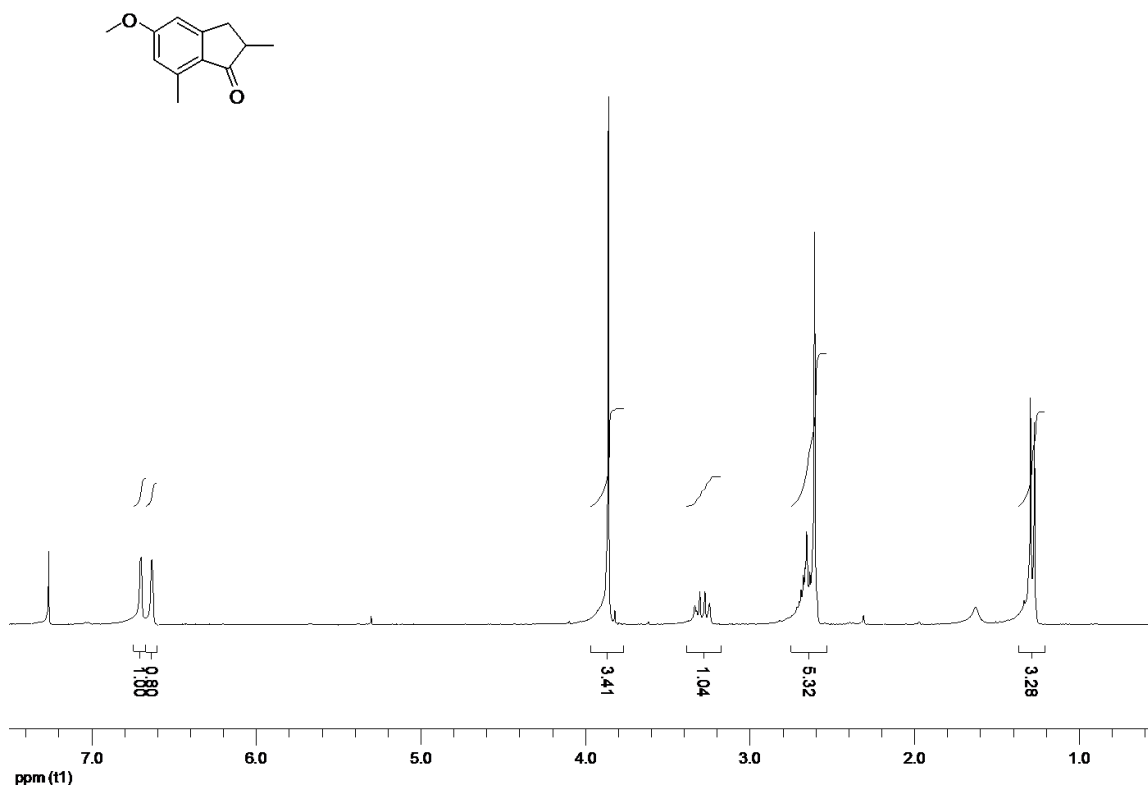


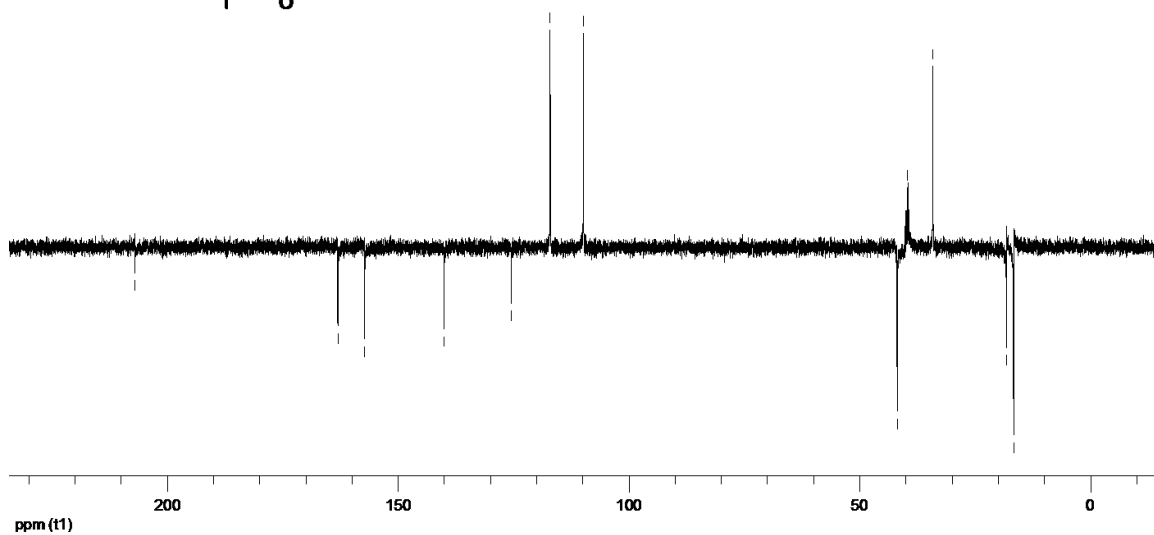
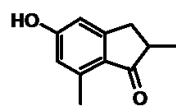
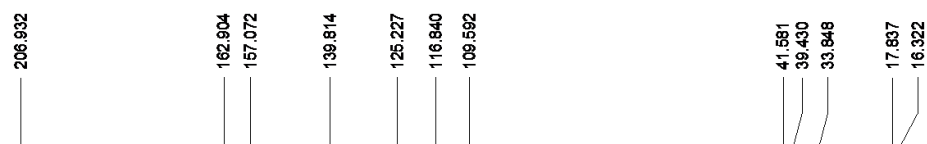
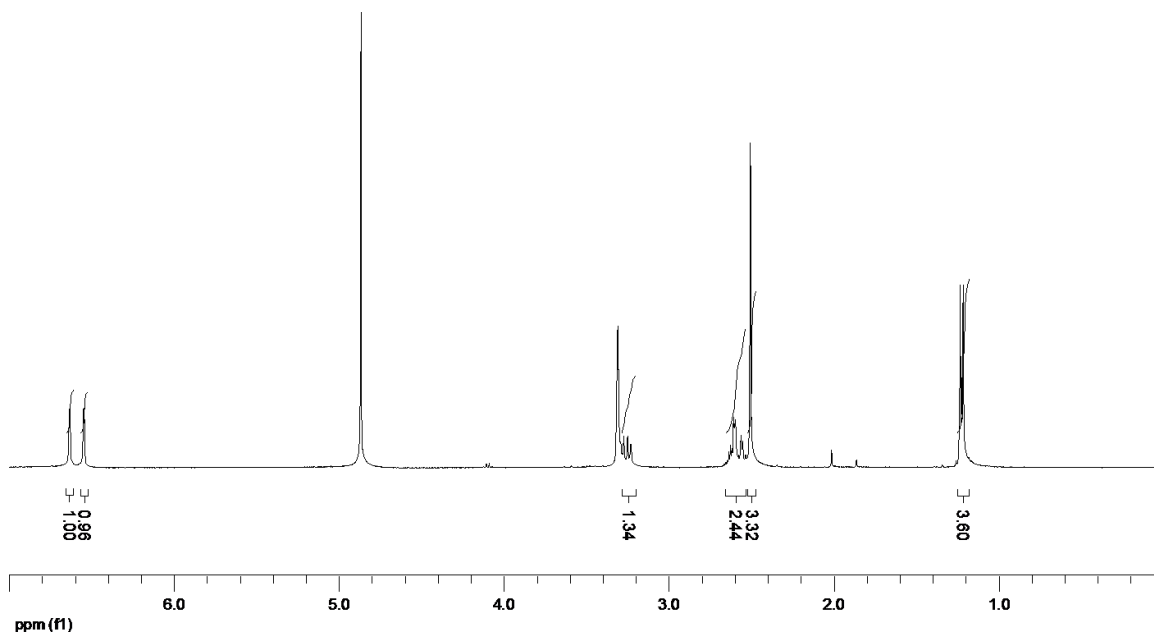
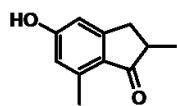
Figure S10: X-ray photoelectron spectrum of N1s core level region of the azide monolayer (**SAM 1**) before (upper panel) and after (lower panel) 1,3-dipolar cycloaddition of the 1-legged alkyne motor **M4**.

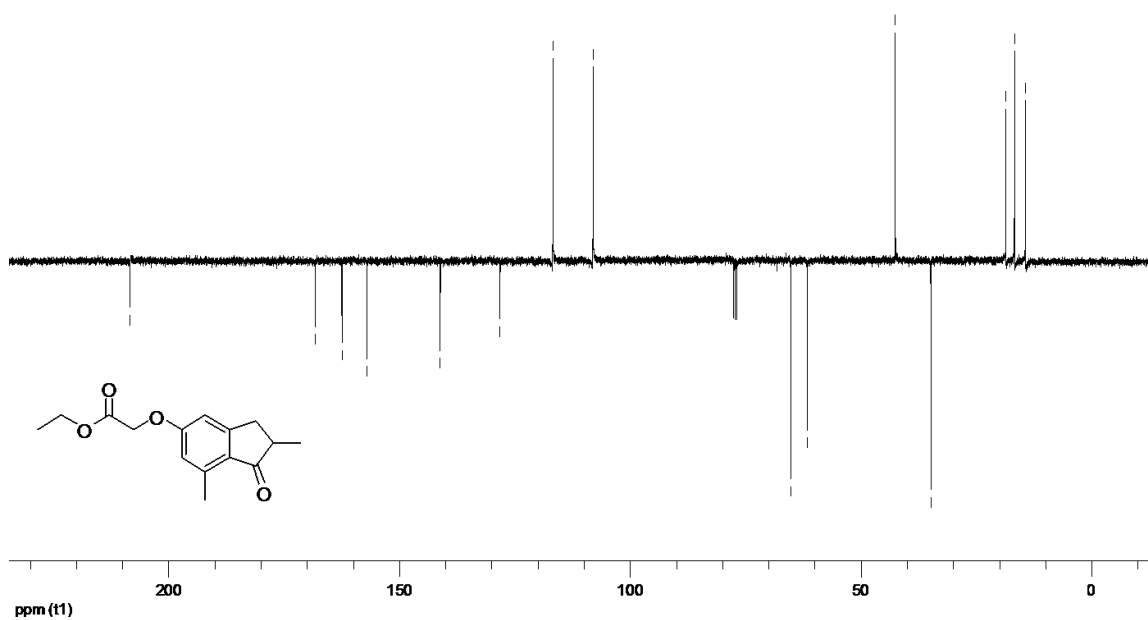
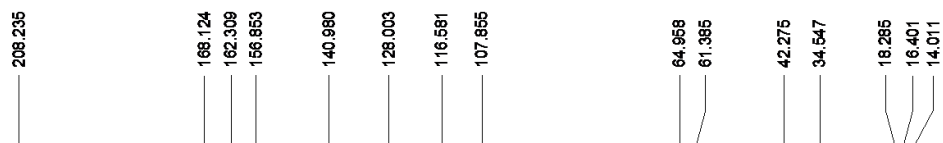
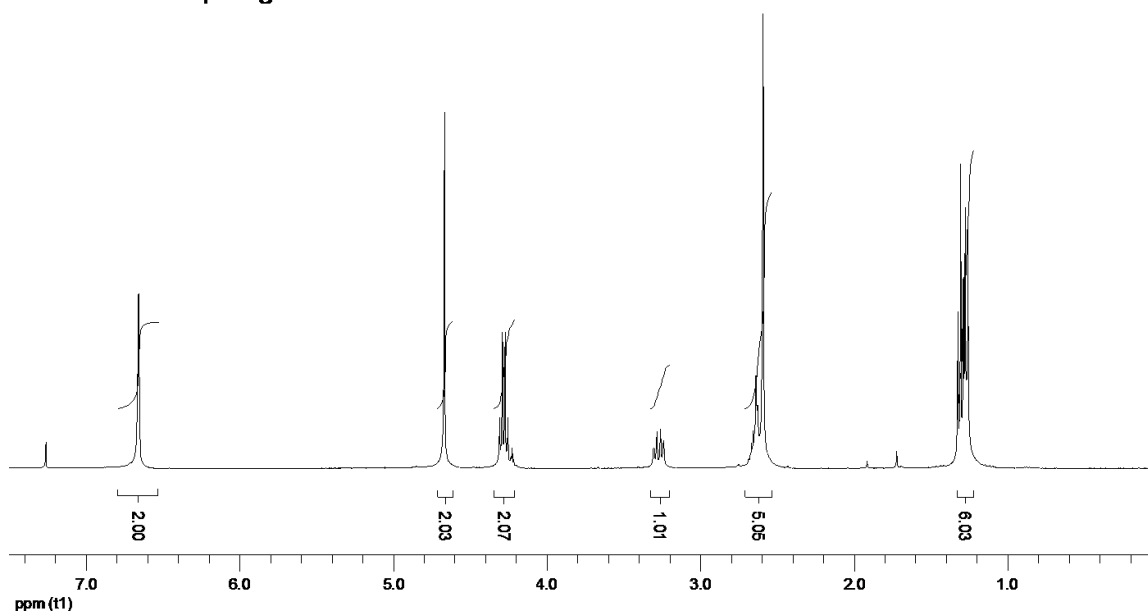
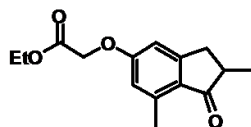
Notes and references

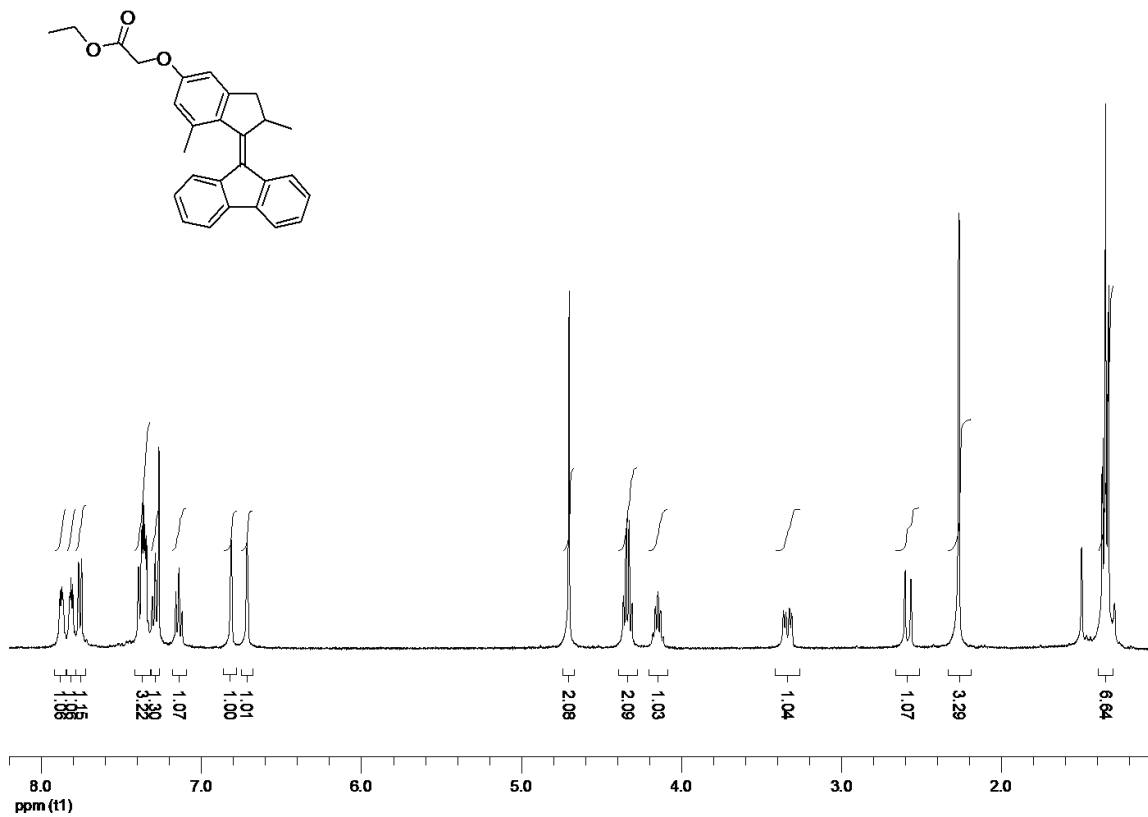
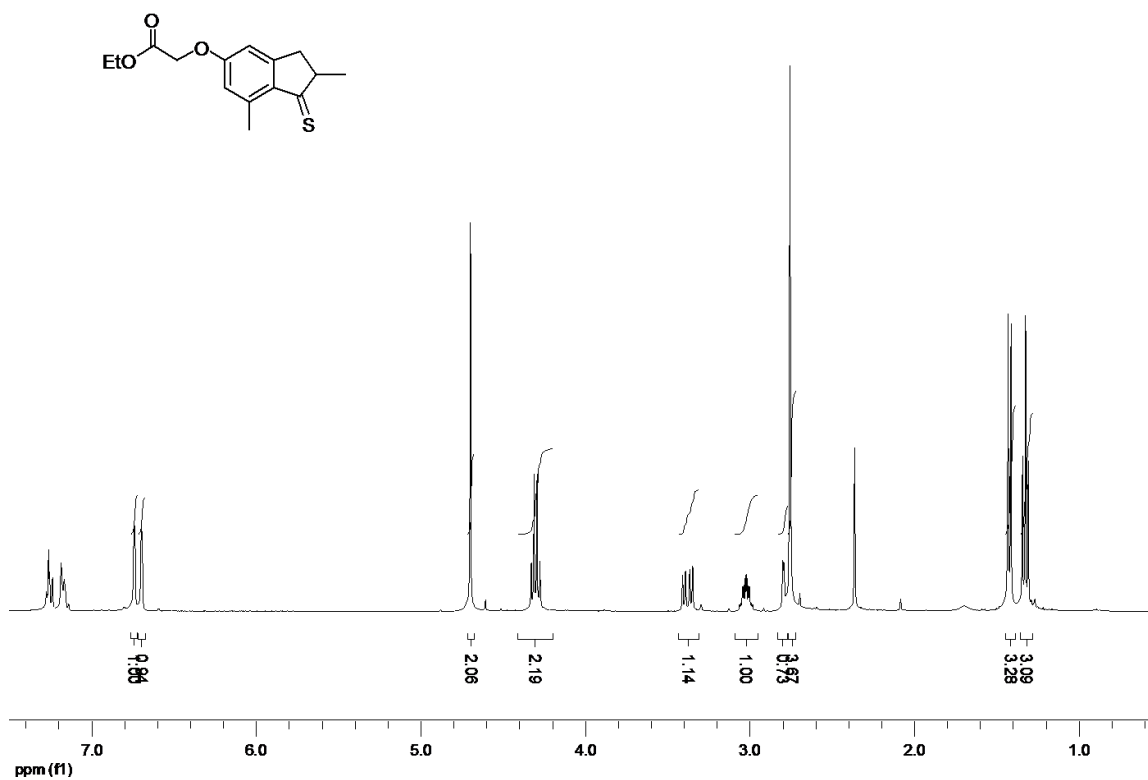
- (1) For the synthesis of **M1** see: G. London, G. T. Carroll, T. Fernandez Landaluce, M. M. Pollard, P. Rudolf, B. L. Feringa, *Chem. Commun.* 2009, 1712.
- (2) For the synthesis of diazofluorenone see: J. Vicario, M. Walko, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* 2006, **128**, 5127.
- (3) D. Briggs, M. P. Seah (Ed.) *Practical Surface Analysis by Auger and X-ray Photoemission spectroscopy*, John Wiley & Sons Ltd.: Chichester 1983.
- (4) J.K. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, Inc., 1995.
- (5) E. W. Wollman, D. Kang, C. D. Frisbie, I. M. Lorkovic, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1994, **116**, 4395.
- (6) J. P. Collman, N. K. Devaraj, T. P. A. Eberspacher, and C. E. D. Chidsey, *Langmuir*, 2006, **22**, 2457.
- (7) A. Devadoos and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 2007, **129**, 5370.

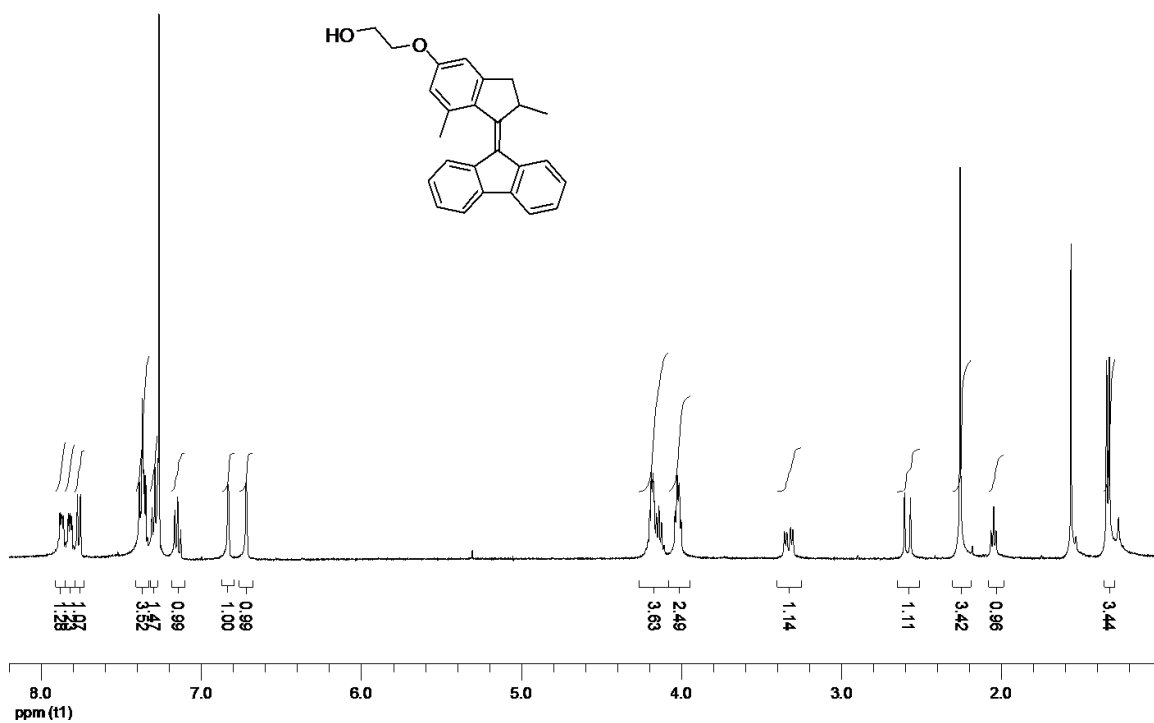
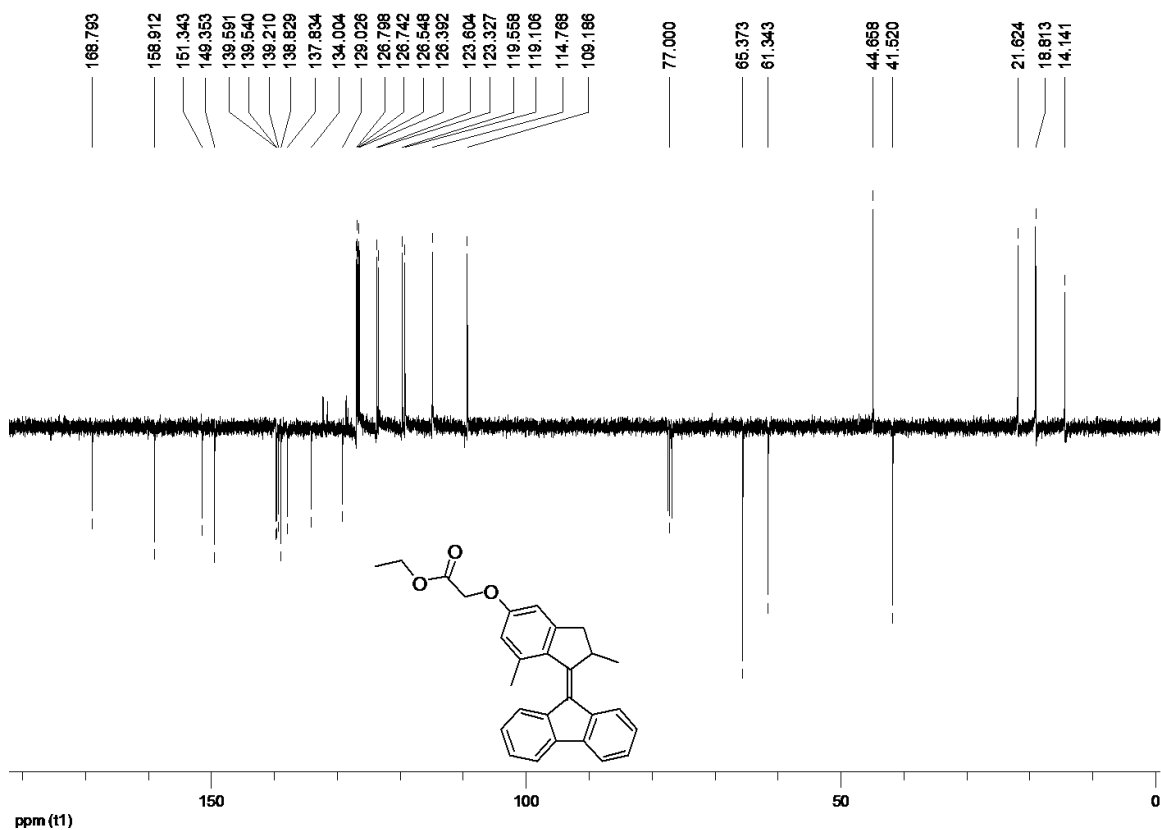
NMR Spectra

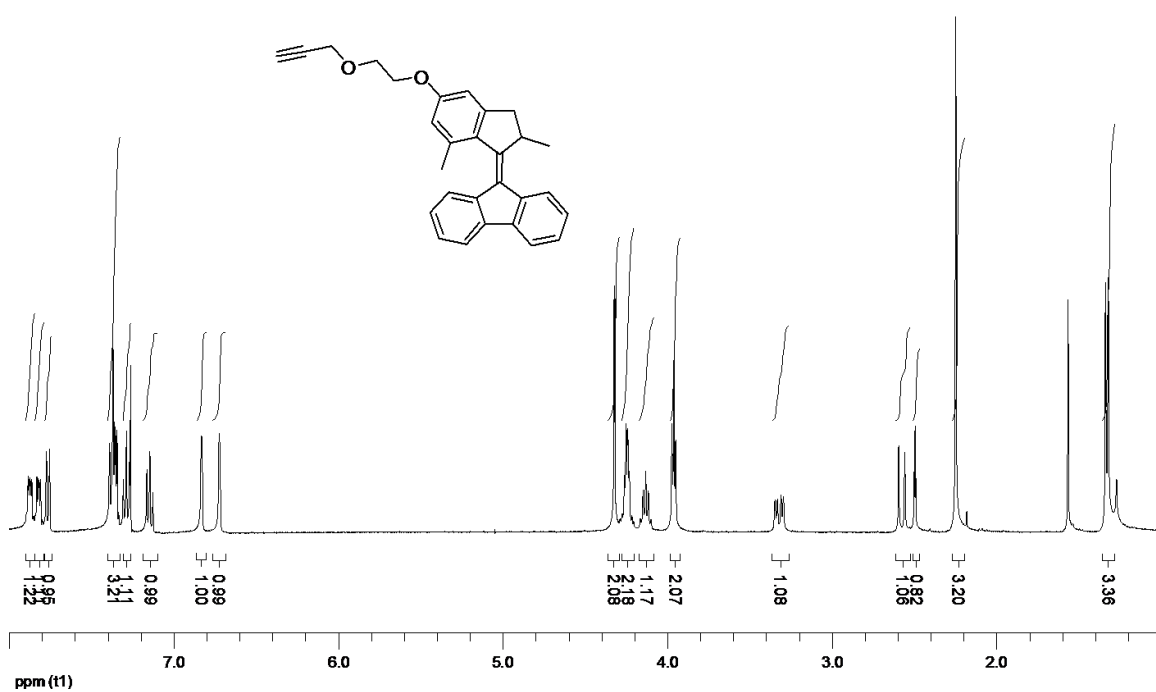
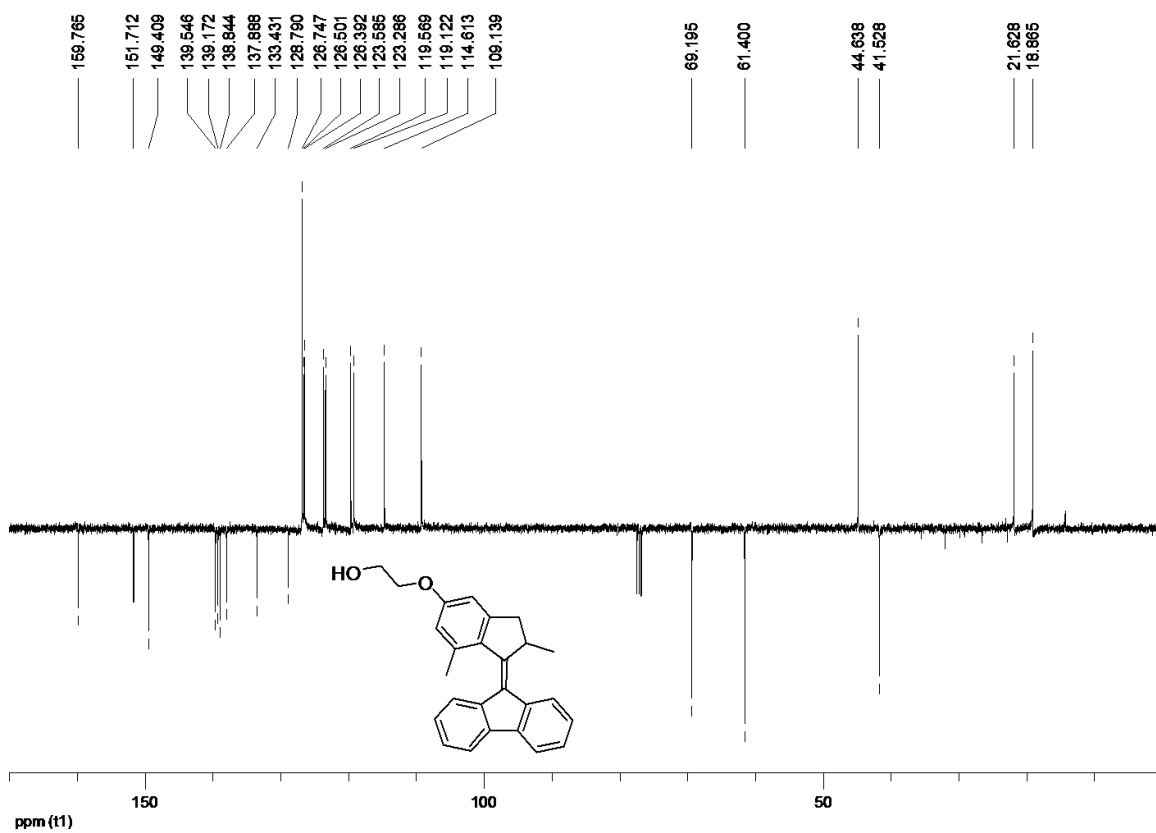


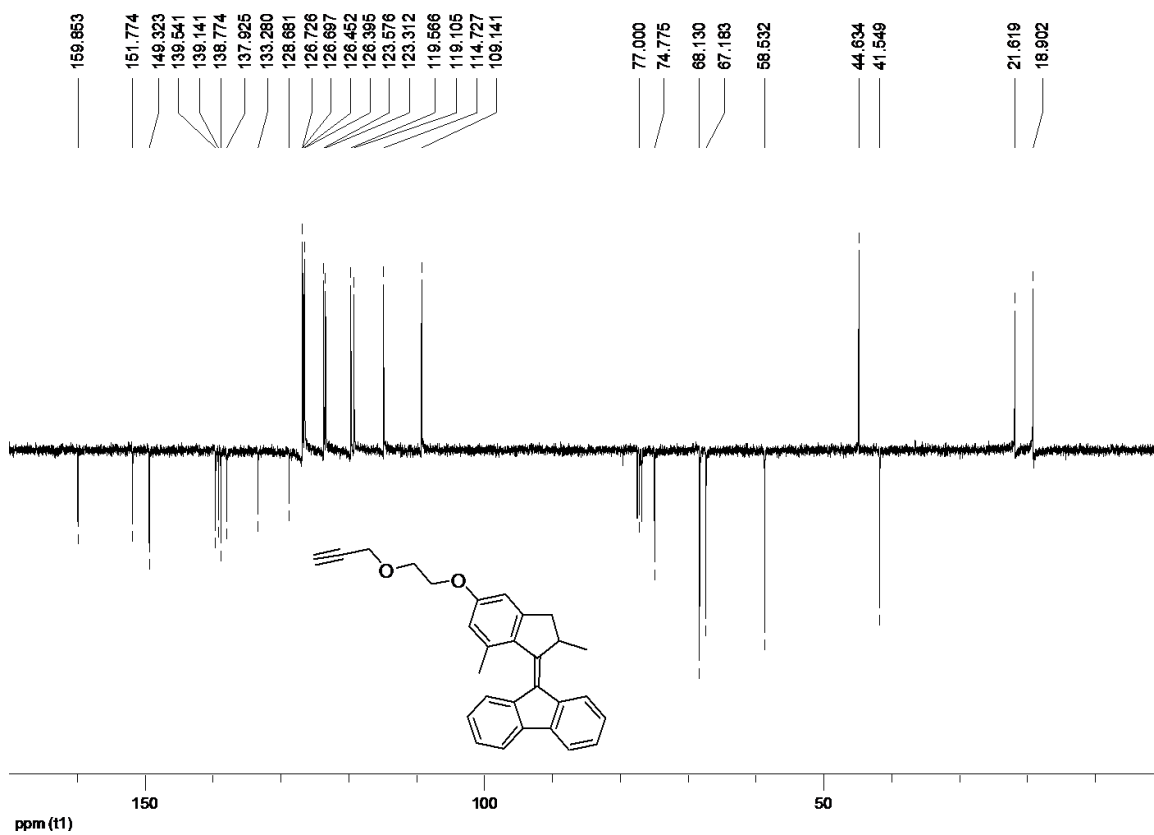


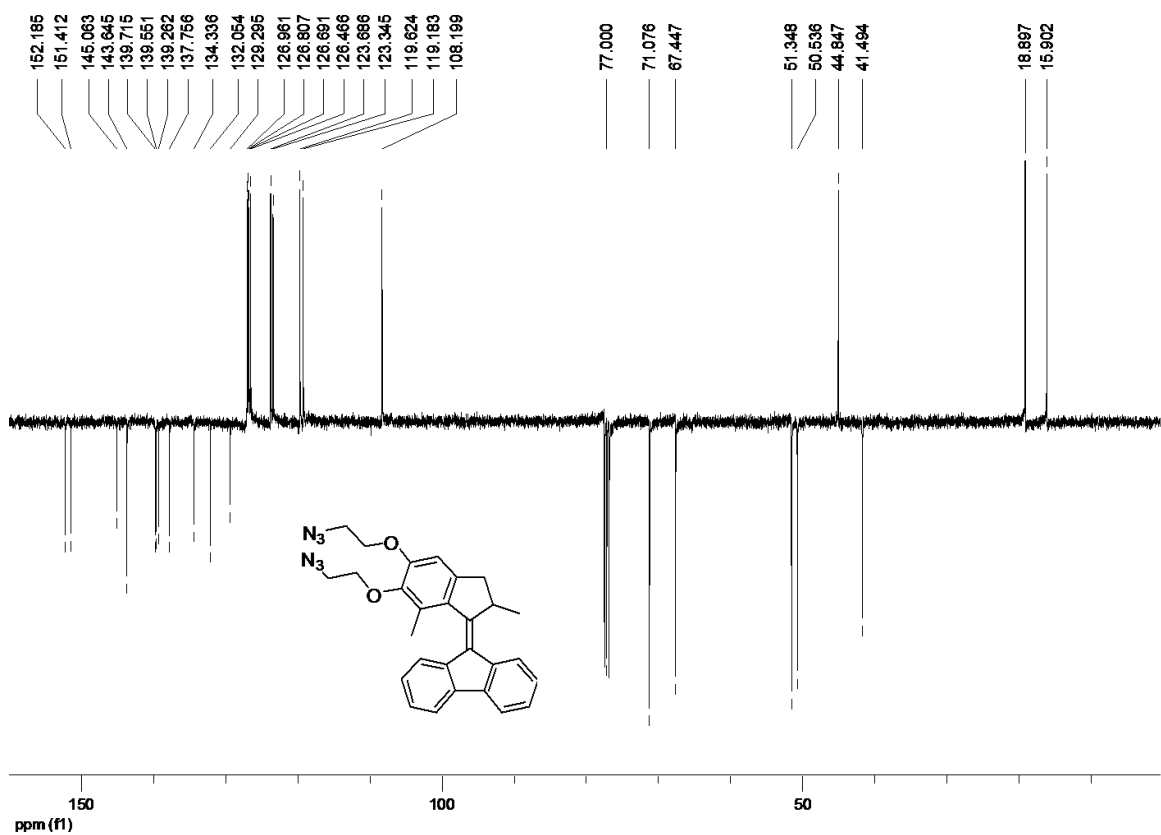
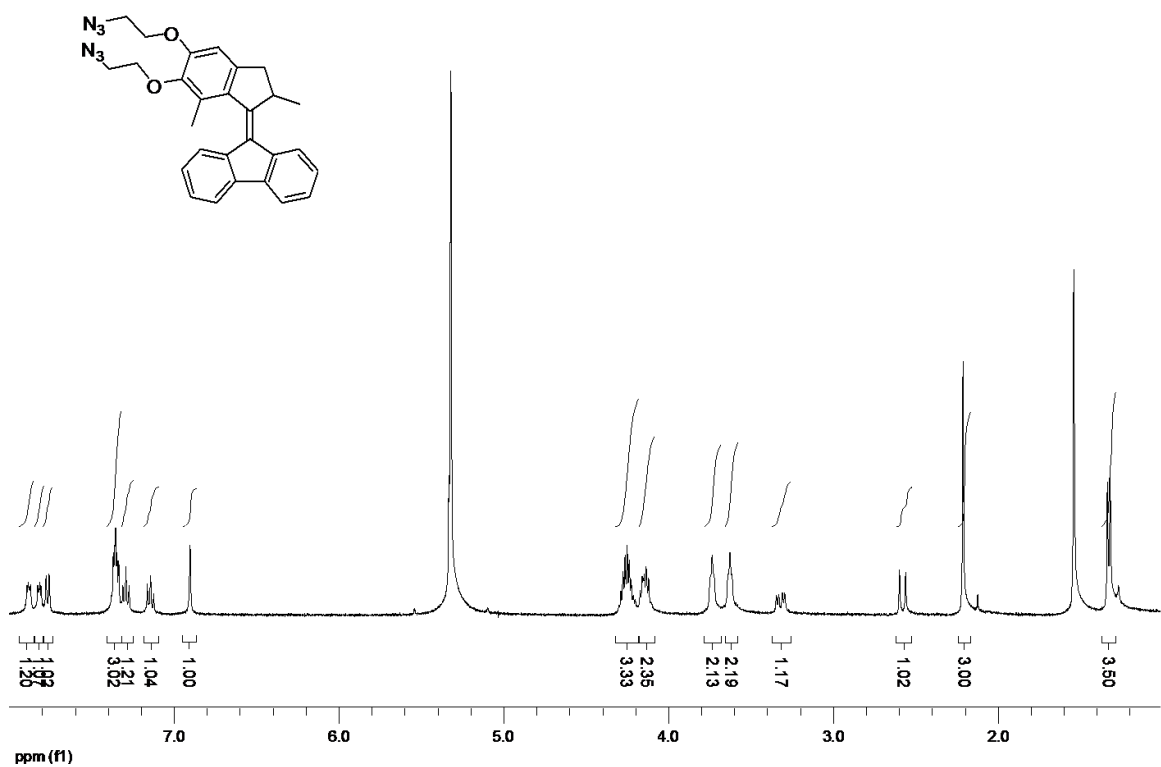


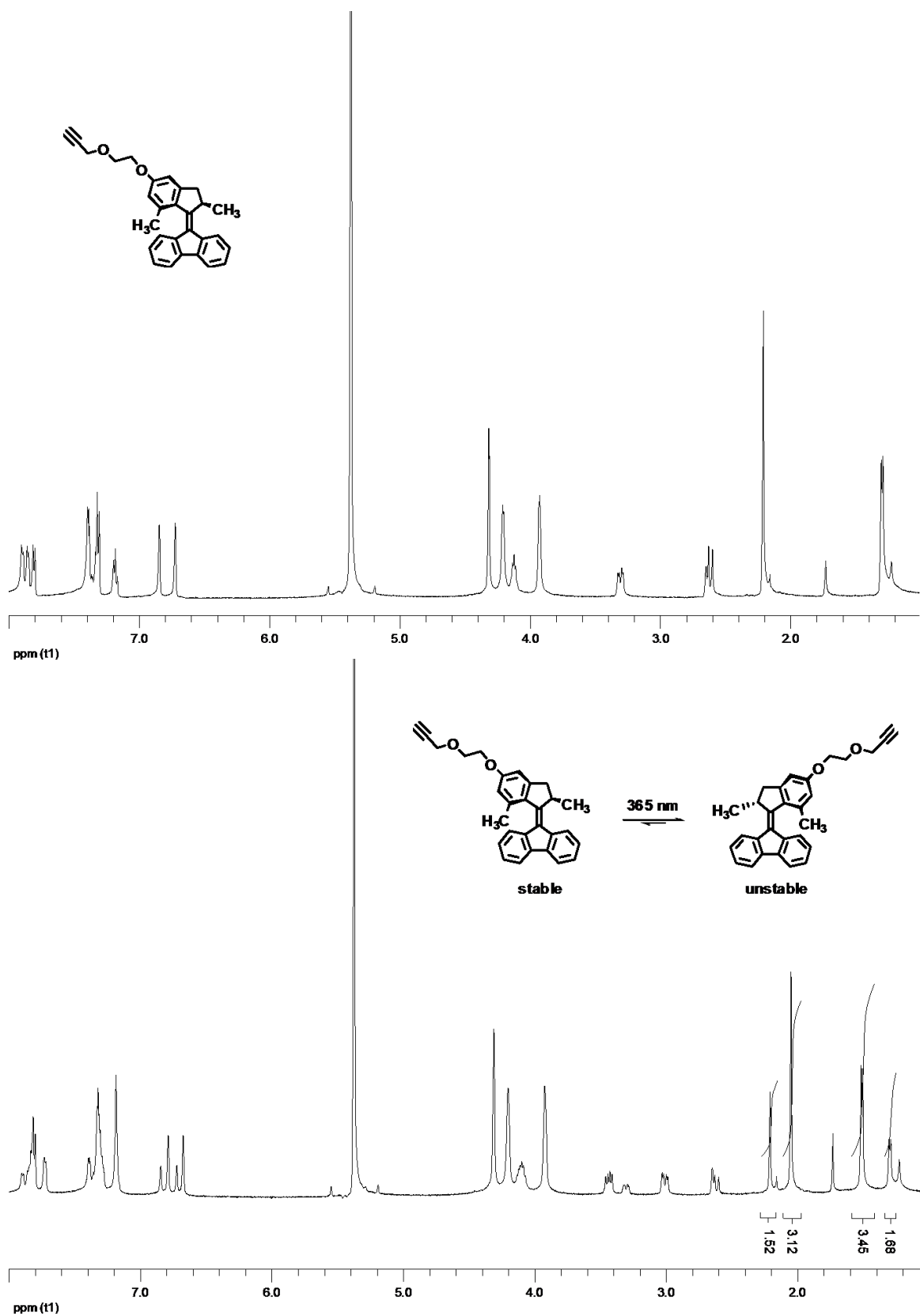




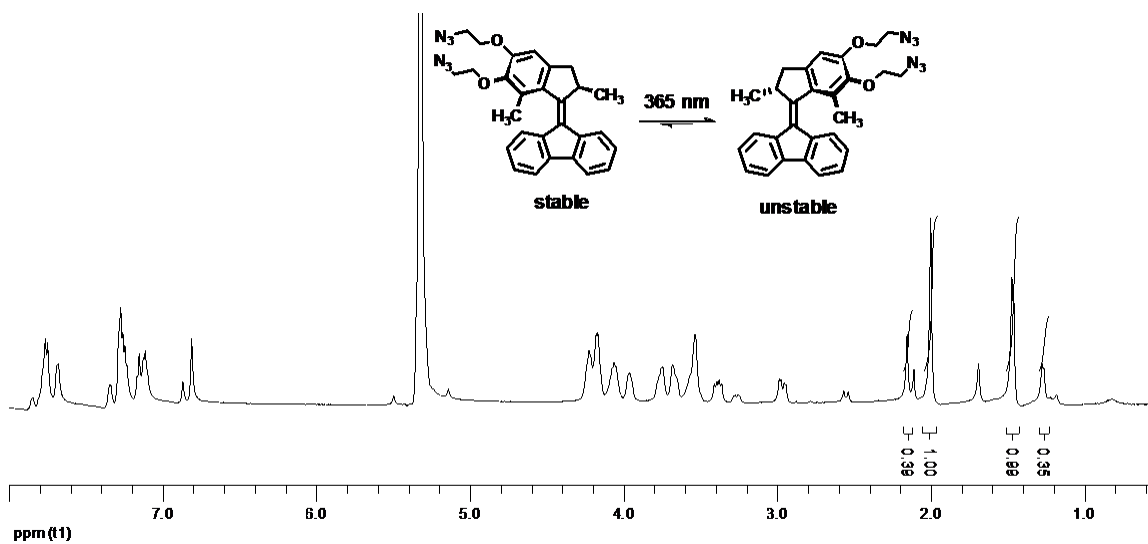
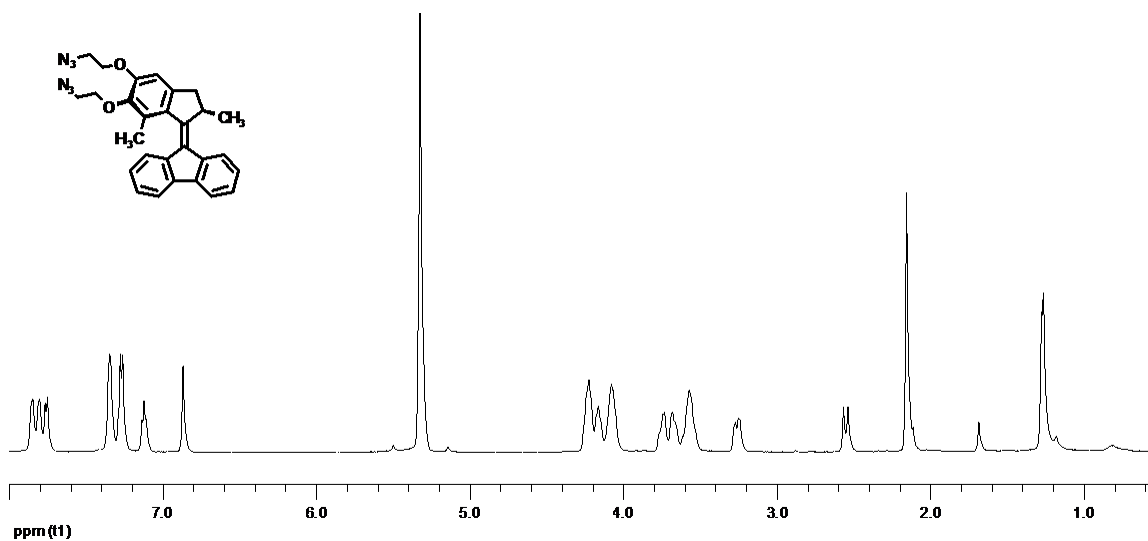








¹H-NMR spectrum of **M4** (500 MHz, CD₂Cl₂ -50°C) and the photostationary state mixture ($\lambda_{\text{max}} = 365 \text{ nm}$) of stable-**M4** and unstable-**M4** (500 MHz, CD₂Cl₂ -50°C)



^1H -NMR spectrum of **M3** (500 MHz, CD_2Cl_2 -50°C) and the photostationary state mixture ($\lambda_{\text{max}} = 365 \text{ nm}$) of stable-**M3** and unstable-**M3** (500 MHz, CD_2Cl_2 -50°C)